

Title: DEVELOPMENT OF HIGH ACTIVITY, COAL-DERIVED, PROMOTED CATALYTIC SYSTEMS FOR NO_x REDUCTION AT LOW TEMPERATURES (DE-FG22-97PC97267)

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Abstract

Background & Objectives. This project is directed at an investigation of catalytic NO_x reduction mechanisms on coal-derived, activated carbon supports at low temperatures (300°C-450°C). Promoted carbon systems offer some potentially significant advantages for heterogeneous NO_x reduction. These include: low cost; high activity at low temperatures, to minimize carbon loss; oxygen resistance; and a support material which can be engineered with respect to porosity, transport and catalyst dispersion characteristics.

The project is currently focused on two promising systems - potassium; and Co/Ni-rare earth oxide-Pt, which have both been shown to be effective for NO reduction at low temperatures, with low carbon loss. In particular, the focus is on the investigation of : (1) a novel, “two-stage” process for the complete reduction of NO to N₂ and O₂ via N₂O as an intermediate; and (2) the use of H₂ and CO reducing agents in conjunction with the promoted carbon systems.

In order to develop and optimize these approaches, however, the fundamental mechanisms responsible for NO_x reduction in these catalytic systems must be better understood and quantified. In this regard, various techniques that have been developed in our laboratory to investigate carbon reactivity will be applied to accomplish this objective. These include temperature programmed reaction (TPR), and post-reaction/chemisorption temperature programmed desorption (TPD), and intermittent temperature programmed desorption (ITPD) methods.

Highlight Accomplishments. Since the recent inception of the project, the following has been accomplished:

(1) An MS-TGA (mass spectrometric-thermogravimetric analysis) apparatus, which is one of the primary instruments that will be used in these studies, is being modified to the specific requirements of this project. A NO_x chemiluminescence analyzer has been added to the instrument to monitor NO_x concentrations in the feed and product streams. In addition, the computer control and data acquisition system, has been updated and modified to accommodate the requirements of the specific types of experiments planned. Some of these updates are still in progress, and should be completed late this spring.

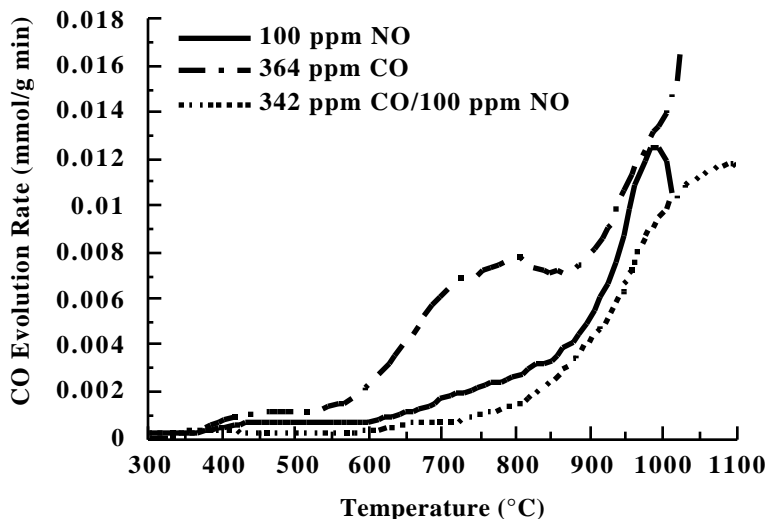
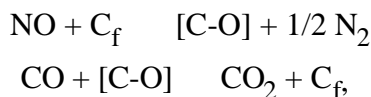


Figure 1. Thermal evolution at 70K/min of surface oxygen (as CO) from phenolic resin char oxidized in NO, CO, and NO+CO in a packed bed reactor.

(2) Studies of the effects of NO and CO in the gas phase on intermediate oxygen surface complex populations on the carbon have also been conducted. Phenolic resin char (PRC) (0.25 g) was oxidized in a packed bed reactor (4 mm x 2.5 cm), with NO alone, CO alone, and NO+CO in 100 ml/min of helium for 2h at 800°C. Samples of this carbon bed material were then subject to temperature programmed desorption in the MS-TGA apparatus at 70K/min in flowing ultrahigh purity helium. Some example results are presented in Figure 1. As shown, with just NO in the flow, relatively little surface oxygen was evolved at temperatures less than 800°C, with a maximum centered at about 980°C. With only CO in the flow, the carbon surface accumulated considerably more oxygen, especially below 800°C, and no maximum was observed, with CO evolution still increasing at the maximum temperature. This additional surface oxygen is attributable to direct CO chemisorption, and perhaps some reverse Boudouard reaction. When both NO and CO were fed together, however, the oxygen surface complex population was observed to decrease to its lowest levels and the maximum in the evolution rate was shifted up to about 1100°C. These results suggest that CO participates in the reduction of NO *via* reaction with oxygen surface complexes; e.g.,



where [C-O] is an intermediate oxygen surface complex, and C_f is a free active carbon site. These studies are intended to establish the mechanism of gas phase reducing agents on heterogeneous NO reduction.

(3) Work has continued on the application of contrast matching, small angle neutron scattering to the characterization and development of char porosity. Contrast matching with perdeuterated toluene was used to discriminate between inaccessible and inaccessible porosity in Pittsburgh #8 coal char and PRC, for which the mechanisms of porosity evolution were shown to be quite different. Upon progressive activation, Pittsburgh #8 coal char widens existing porosity and develops new porosity, while PRC progressively opens existing, previously inaccessible porosity *via* selective burn-off of amorphous carbon which initially blocks the underlying intrinsic porosity. This technique is being investigated from the point of view of porosity characterization of the carbon support materials for NO_x reduction systems.

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Articles and Presentations

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- P.J. Hall, M.M. Antxustegi, and J.M. Calo, "The Use of Contrast Matching Small Angle Neutron Scattering Techniques to Monitor Closed Porosity in Carbons," in press, *J. Coll. Intf. Sci.*, 1998.
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